

# Non-Kramers freezing and unfreezing of tunneling in the biaxial spin model

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**Abstract.** – The ground state tunnel splitting for the biaxial spin model in the magnetic field,  $\mathcal{H} = -DS_x^2 + ES_z^2 - g\mu_B S_z H_z$ , has been investigated using an instanton approach. We find a new type of spin instanton and a new quantum interference phenomenon associated with it: at a certain field,  $H_2 = 2SE^{1/2}(D+E)^{1/2}/(g\mu_B)$ , the dependence of the tunneling splitting on the field switches from oscillations to a monotonic growth. The predictions of the theory can be tested in Fe<sub>8</sub> molecular nanomagnets.

During the last years much effort, both theoretical and experimental, has been devoted to the study of macroscopic quantum tunneling (MQT) in spin systems[1, 2]. Crystals formed by weakly interacting identical magnetic molecules, like Mn<sub>12</sub>-acetate and an octanuclear iron cluster Fe<sub>8</sub>, have been the objects of most intensive recent research. EPR [3] and neutron scattering [4] data show that an Fe<sub>8</sub> cluster can be described by the biaxial spin Hamiltonian,

$$\mathcal{H} = -DS_x^2 + ES_z^2 - g\mu_B \mathbf{S} \cdot \mathbf{H} , \quad (1)$$

where  $S = 10$ ,  $D \approx 0.23$ – $0.27$  K, and  $E \approx 0.093$  K [3]. Macroscopic magnetic measurements [5] have revealed resonant spin tunneling in Fe<sub>8</sub>, confirming the above model and values of the constants. At  $H = 0$  this model has been studied by a number of authors[6, 7, 8, 9]. The tunnel splitting  $\Delta$  of the ground state in the case  $H \neq 0$  has been theoretically studied using the instanton method by Garg [10], who discovered an interesting topological effect: oscillation of  $\Delta$  on the magnetic field applied along the hard magnetization axis. Such oscillations have been recently observed in Fe<sub>8</sub> by Wernsdorfer and Sessoli [11]. The origin of this effect is in the quantum interference of different instanton paths, suggested earlier, within the context of MQT, by Loss, DiVincenzo, and Grinstein [12] and by von Delft and Henley[13]. This oscillatory behaviour has also been derived using standard perturbation theory by Weigert[14]. The model of Garg has elucidated the fact that the freezing of tunneling need not be related

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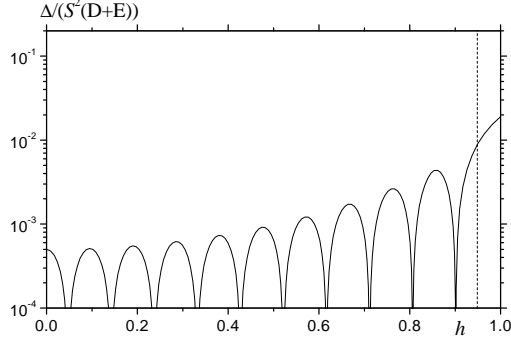


Fig. 1 – The tunnel splitting  $\Delta$  as a function of field  $h$  at  $S = 10$  and  $\lambda = 0.1$ . Dashed line marks the unfreezing field  $h_2 = 0.949$ .

to Kramers's degeneracy. To illustrate his point, Garg studied the field range  $0 < h < h_2 = (1 - \lambda)^{1/2}$ , where  $h = H/H_c$ ,  $H_c = 2S(D + E)/(g\mu_B)$  is the critical field at which the energy barrier disappears, and  $\lambda = D/(D + E)$ . In that field range the tunneling is quenched whenever [10]

$$h = h_2(S - n - 1/2)/S, \quad n = 0, 1, \dots, 2S - 1. \quad (2)$$

This was discovered before the relevant system, Fe<sub>8</sub>, was known. Meantime, for Fe<sub>8</sub>  $\lambda \approx 0.71$ – $0.75$  and, thus, the above field range covers only the lower half of the range,  $0 < H < H_c \approx 4.8$ – $5.5$  T, available for the tunneling studies. In this Letter we have considered the remaining field range,  $h_2 < h < 1$ , and found another interesting topological effect: switching from oscillations to the monotonic growth of the tunnel splitting on the field. We then give explanation to such a behavior within a continuous spin model containing the Wess-Zumino-Berry term[15]. Hamiltonian (1) has been recently studied by Kou et al.[16] who found exact instantons at  $h < h_2$  but did not attempt to solve the problem in the field range  $h_2 < h < 1$ . We show that there exists a new type of spin instanton in that range, that involves motion in both imaginary and real time, which is ultimately responsible for the above peculiar dependence of the tunnel splitting on the field. Complex-time instantons have been used for some time to study barrier penetration effects using the path integral formalism[17, 18, 19]. To our knowledge, though, this is the first time that such a mixed-time trajectory is needed in the study of tunneling in spin systems. Garg's and our predictions can be quantitatively tested, without any fitting parameters, in experiments on Fe<sub>8</sub>.

Before studying instantons we will demonstrate the reality of the effect by performing the numerical diagonalization of the Hamiltonian (1) for  $S = 10$  in the field applied along the hard axis  $Z$  (see also ref. [20]). Figures 1–3 show the results of numerical computations of the ground state tunnel splitting as a function of  $h$  for three different values of  $\lambda$ : small  $\lambda$ , intermediate  $\lambda$  that corresponds to Fe<sub>8</sub>, and large  $\lambda$ . It can be clearly seen from the figures that Garg's oscillations exist below a certain field  $H_2$ . Above that field there are no oscillations; the tunnel splitting grows linearly with the field. The value of  $H_2$  increases with decreasing  $\lambda$ . Below, we obtain this effect via instanton method and show that the crossover field is given by  $h_2(\lambda) = (1 - \lambda)^{1/2}$ .

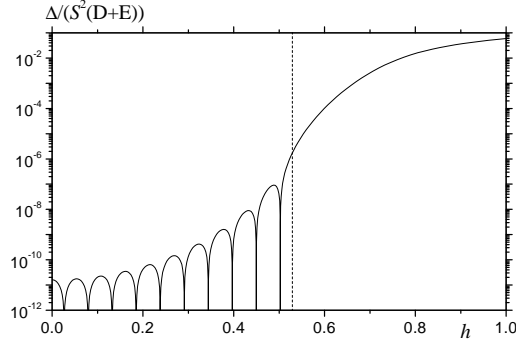


Fig. 2 – The tunnel splitting  $\Delta$  as a function of field  $h$  for  $\text{Fe}_8$ ,  $S = 10$  and  $\lambda = 0.72$ . Dashed line marks the unfreezing field  $h_2 = 0.529$ .

In the continuous approach the tunnel splitting can be computed as the functional integral

$$\oint \mathcal{D}[\cos \theta(t)] \mathcal{D}[\phi(t)] \exp \left( \frac{i}{\hbar} \int dt \mathcal{L}[\theta(t), \phi(t)] \right) \quad (3)$$

over closed trajectories which describe motion of a fixed-length vector of the magnetic moment  $\mathbf{M}$  in spherical coordinates  $(\theta(t), \phi(t))$ . Here  $\mathcal{L}$  is the Lagrangian of the magnetic system,

$$\mathcal{L} = \frac{M}{\gamma} (\cos(\theta) - 1) \dot{\phi} - \mathcal{H}(\theta, \phi), \quad (4)$$

and  $\mathcal{H}$  is the energy of the system, which includes the magnetic anisotropy and the Zeeman term,

$$\mathcal{H}(\theta, \phi) = -\frac{1}{2} M k_{\parallel} \sin^2(\theta) \cos^2(\phi) + \frac{1}{2} M k_{\perp} \cos^2(\theta)$$

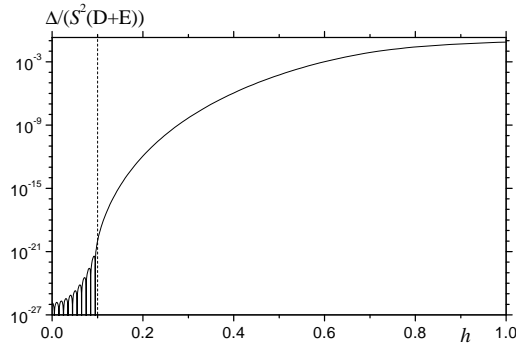


Fig. 3 – The tunnel splitting  $\Delta$  as a function of field  $h$  at  $S = 10$  and  $\lambda = 0.99$ . Dashed line marks the unfreezing field  $h_2 = 0.1$ .

$$-MH \cos(\theta) + \frac{1}{2}M \left( k_{\parallel} + \frac{H^2}{k_{\perp} + k_{\parallel}} \right). \quad (5)$$

Here  $\gamma = g\mu_B/\hbar$  is the gyromagnetic ratio,  $H$  is the external field, and  $k_{\perp}$  and  $k_{\parallel}$  are the hard and easy anisotropy constants, correspondingly. The correspondence with the parameters of the Hamiltonian (1) is the following

$$k_{\parallel} = \frac{2SD}{g\mu_B}, \quad k_{\perp} = \frac{2SE}{g\mu_B}, \quad H_c = k_{\perp} + k_{\parallel},$$

$$\mathbf{S} = \frac{\mathbf{M}}{\hbar\gamma}, \quad \lambda = \frac{k_{\parallel}}{k_{\parallel} + k_{\perp}}. \quad (6)$$

For  $H < H_c$ , the magnetic energy  $\mathcal{H}(\theta, \phi)$  has two equivalent minima at  $\phi = 0, \pi$  with  $\cos(\theta) = H/H_c$ . A constant has been added to make the energy of the minima zero. The following observation is relevant to the calculation provided below. The energy (5), besides having the minima mentioned above, also has two equivalent extrema at  $\phi = \pm\pi/2$  and  $\cos\theta = h/h_1$ , where  $h_1 = 1 - \lambda$ . At  $0 < h < h_1$  these are the maxima of the energy. They would become local minima of the energy at  $h_1 < h < h_2$  and global minima at  $h_2 < h < 1$  if one allowed for complex  $\theta$ , because  $\cos\theta = h/h_1 > 1$  in that field range. We shall see that this is the case for the effective potential in the quantum problem.

After Gaussian integration over  $\cos(\theta)$  in eq. (3), the remaining functional integral over  $\phi$  contains the imaginary-time effective action

$$\begin{aligned} \frac{I}{\hbar} &= \frac{1}{\hbar} \int d\tau \mathcal{L}_E = -iS \int d\phi [A(\phi) - 1] \\ &\quad + S\lambda^{1/2} \int d\tau' \left[ \frac{1}{2} M(\phi) \dot{\phi}_{\tau'}^2 + V(\phi) \right], \end{aligned} \quad (7)$$

where  $\mathcal{L}_E = -\mathcal{L}(t \rightarrow -i\tau)$  is the Euclidean Lagrangian, and  $\tau' = \tau\gamma[k_{\parallel}(k_{\perp} + k_{\parallel})]^{1/2}$  is the dimensionless imaginary time. The functions  $A(\phi)$ ,  $M(\phi)$  and  $V(\phi)$  are given by

$$A(\phi) = \frac{h}{1 - \lambda \sin^2(\phi)}, \quad (8)$$

$$M(\phi) = \frac{1}{1 - \lambda \sin^2(\phi)}, \quad (9)$$

and

$$V(\phi) = \frac{1}{2} \sin^2(\phi) \left[ 1 - \frac{h^2}{1 - \lambda \sin^2(\phi)} \right]. \quad (10)$$

The action (7) is equivalent to that describing the motion of a particle of mass  $M(\phi)$  in an inverted scalar potential  $-V(\phi)$  and a “vector” potential  $A(\phi) - 1$ . The shape of the potential  $V(\phi)$  for three different ranges of the field is shown in fig. 4. For  $h < h_1 = 1 - \lambda$ , the potential looks like a regular barrier between  $\phi = 0$  and  $\phi = \pi$ , with a maximum at  $\phi = \pi/2$ . For  $h_1 < h < h_2 = (1 - \lambda)^{1/2}$ , the maximum at  $\phi = \pi/2$  becomes a local minimum, though still higher than the global minima at  $\phi = 0, \pi$ . For  $h_2 < h < 1$ , the minimum at  $\phi = \pi/2$  becomes the global minimum.

For  $0 < h < h_2$  one can find the imaginary-time instanton trajectories for the particle moving from  $\phi = 0$  to  $\phi = \pm\pi$  in the inverted potential. For these trajectories, the first integral in eq. (7) gives an imaginary Wess-Zumino-Berry contribution to the action,

$$\frac{i}{\hbar} S I_{WZB}^{\pm} = -iS \int d\phi [A(\phi) - 1] = \pm i\pi S \left( 1 - \frac{h}{h_2} \right). \quad (11)$$

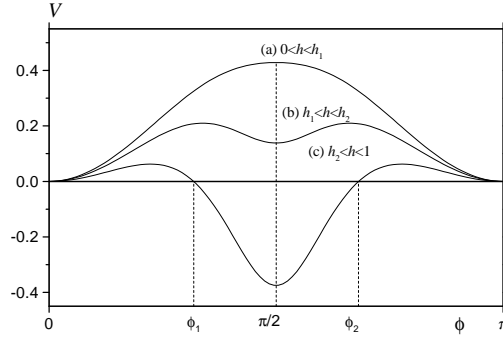


Fig. 4 – The potential  $V(\phi)$  at  $\lambda = 0.72$  ( $h_1 = 0.28$  and  $h_2 = 0.529$ ) for three different ranges of the field. The chosen fields are: (a)  $h = 0.2$ , (b)  $h = 0.45$ , and (c)  $h = 0.7$ .

The interference of these two trajectories in the functional integral gives a factor

$$e^{\frac{i}{\hbar} I_{WZB}^+} + e^{\frac{i}{\hbar} I_{WZB}^-} = 2 \cos \left[ \pi S \left( 1 - \frac{h}{h_2} \right) \right], \quad (12)$$

which is responsible for the non-Kramers freezing of tunneling at fields satisfying eq. (2)[10].

However, at  $h_2 < h < 1$ , one cannot find a trajectory in imaginary-time connecting 0 and  $\pi$ . There seems to be instead a bounce trajectory from  $\phi = 0$  to  $\phi_1$  and from  $\phi_2$  to  $\pi$ , where  $\sin^2(\phi_{1,2}) = (1 - h^2)/\lambda$ . We then consider the instanton given by the trajectory which consists of three parts:

1. motion in imaginary time from 0 to  $\phi_1$ ,
2. motion in real time from  $\phi_1$  to  $\phi_2$ ,
3. motion in imaginary time from  $\phi_2$  to  $\pi$ ,

and another instanton given by the trajectory going in the opposite direction. It is clear from the shape of the potential that all three parts of the trajectory join smoothly, because  $\phi(\tau)$  and  $\dot{\phi}_\tau(\tau)$  coincide at the joints. Note that the real-time part of the trajectory still corresponds to the virtual rotation of the magnetic moment, because for that part of the trajectory  $\cos(\theta) > 1$ , as can be seen from the classical equations of motion that follow from the Lagrangian (4).

Using the energy conservation

$$\mathcal{H}(\phi, \dot{\phi}_{\tau'}) = \frac{1}{2} M(\phi) \dot{\phi}_{\tau'}^2 - V(\phi) = 0, \quad (13)$$

one obtains

$$\dot{\phi}_{\tau'}^2 = \frac{2V(\phi)}{M(\phi)} = (1 - h^2) \sin^2(\phi) \left[ 1 - \frac{\lambda}{1 - h^2} \sin^2(\phi) \right]. \quad (14)$$

This can be used to compute the second integral in eq. (7). For  $h_2 < h < 1$ , the real part of the imaginary-time action is given by the contribution of the bounce trajectories from 0 to  $\phi_1$

and from  $\phi_2$  to  $\pi$ . Integration gives

$$\begin{aligned} \text{Re} \left( \frac{I}{\hbar} \right) &= 2S\lambda^{1/2} \int_{[0, \phi_1] \cup [\phi_2, \pi]} d\phi [2M(\phi)V(\phi)]^{1/2} \\ &= 4S \left[ z - \left( \frac{1}{a^2} + 1 \right)^{1/2} \tanh^{-1} \left( \frac{a^2 - b^2}{1 + a^2} \right)^{1/2} \right], \end{aligned} \quad (15)$$

where

$$\begin{aligned} z &= \cosh^{-1} \left( \frac{a}{b} \right), \quad a^2 = \frac{1 - \lambda}{h^2 - (1 - \lambda)}, \\ b^2 &= \frac{1 - \lambda}{\lambda} = \frac{k_{\perp}}{k_{\parallel}}. \end{aligned} \quad (16)$$

Equation (15) is the WKB exponent for the tunnel splitting.

In the uniaxial limit ( $\lambda \rightarrow 1$ ), one obtains

$$\text{Re} \left( \frac{I}{\hbar} \right) = 4S \left[ \cosh^{-1} \left( \frac{1}{h} \right) - (1 - h^2)^{1/2} \right], \quad (17)$$

in full agreement with ref. [21]. This formula is correct in the entire field range  $0 < h < 1$ . In the limit of small barrier [22],  $h = 1 - \epsilon$  with  $\epsilon \rightarrow 0$ , it gives

$$\text{Re} \left( \frac{I}{\hbar} \right) = \frac{8\sqrt{2}}{3} S \epsilon^{3/2}. \quad (18)$$

For  $h < h_2$ , the imaginary part of the action for the trajectory going from  $\phi = 0$  to  $\phi = \pi$  is given solely by the topological term  $(i/\hbar)SI_{WZB}^{\pm}$ . For  $h_2 < h < 1$ , however, we have another contribution coming from the second integral in eq. (7) evaluated for the real-time motion between  $\phi_1$  and  $\phi_2$ . Both contributions combine into

$$\begin{aligned} \text{Im} \left( \frac{I}{\hbar} \right) &= \frac{i}{\hbar} SI_{WZB}^{\pm} \pm S\lambda^{1/2} \int_{\phi_1}^{\phi_2} d\phi [2M(\phi)V(\phi)]^{1/2} \\ &= \frac{i}{\hbar} SI_{WZB}^{\pm} \mp i\pi S \left( 1 - \frac{h}{h_2} \right) = 0. \end{aligned} \quad (19)$$

Remarkably, the real-time motion exactly cancels the contribution of the Wess-Zumino-Berry phase. Consequently, the freezing of tunneling does not occur at high fields ( $h_2 < h < 1$ ) and topological oscillations are suppressed, as confirmed by our numerical diagonalization of the Hamiltonian at  $S = 10$ , figs. 1–3. In each of the figs. 1–3 the field  $h_2$  seem to coincide with the inflexion point on the envelope curve.

Formally, one could argue that at  $h_2 < h < 1$  the instantons connecting the  $\phi = \pm\pi/2$  global minima of the effective potential shown in fig. 4 should be used to compute the tunneling splitting of the ground state. This would be conceptually incorrect, however, because tunneling in the biaxial model occurs between the energy minima  $\phi = 0, \pi$ , which are the only classical energy minima of the energy. Besides, the tunneling splitting computed via the  $\phi = \pm\pi/2$  instantons is different from the one given above and checked through the numerical diagonalization of the Hamiltonian.

One should notice that for  $h_2 < h < 1$  the particle spends finite real time under the barrier, though the motion is still virtual because  $\cos(\theta) > 1$ . This time is given by  $T =$

$2\pi/[\gamma[(1-h^2)k_{\parallel}(k_{\parallel}+k_{\perp})]^{1/2}]$ . It tends to the period of small oscillations around the minimum at  $\phi = \pi/2$  when  $h \rightarrow h_2$ , and diverges when the field approaches the critical value  $h = 1$ . Notice also that complex instantons resembling our instantons have been recently introduced in a rotating black hole problem[23].

Taking the average of the measured values of the parameters[3, 4, 5], we get  $\lambda \approx 0.72$  for Fe<sub>8</sub>, which gives  $h_2 \approx 0.53$ , and  $H_c \approx 5.1$  T. Then the Garg's oscillations must exist at  $H < H_2 \approx 2.7$  T, while above 2.7 T the tunnel splitting must grow monotonically with the field. This prediction can be tested in EPR and inelastic neutron scattering experiments on well oriented crystals of Fe<sub>8</sub>.

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## REFERENCES

- [1] L. GUNTHER and B. BARBARA (Editor), *Quantum Tunneling of Magnetization* (Kluwer, Dordrecht) 1995.
- [2] CHUDNOVSKY E. M. and TEJADA J., *Macroscopic Quantum Tunneling of the Magnetic Moment* (Cambridge University Press) 1998.
- [3] BARRA A.-L., DEBRUNNER P., GATTESCHI D., SCHULZ CH. E. and SESSOLI R., *Europhys. Lett.*, **35** (1996) 133.
- [4] CACIUFFO R., AMORETTI G., MURANI A., SESSOLI R., CANESCHI A. and GATTESCHI D., *Phys. Rev. Lett.*, **81** (1998) 4744.
- [5] SANGREGORIO C., OHM T., PAULSEN C., SESSOLI R. and GATTESCHI D., *Phys. Rev. Lett.*, **78** (1997) 4645.
- [6] ENZ M. and SCHILLING R., *J. Phys. C*, **19** (1986) L711.
- [7] VAN HEMMEN J. L. and SÜTÖ A., *Physica B*, **141** (1986) 37.
- [8] CHUDNOVSKY E. M. and GUNTHER L., *Phys. Rev. Lett.*, **60** (1988) 661.
- [9] GARANIN D. A., *J. Phys. A*, **24** (1991) L61.
- [10] GARG A., *Europhys. Lett.*, **22** (1993) 205.
- [11] WERNSDORFER W. and SESSOLI R., *Science*, **284** (1999) 133.
- [12] LOSS D., DIVINCENZO D. P. and GRINSTEIN G., *Phys. Rev. Lett.*, **69** (1992) 3232.
- [13] VON DELFT J. and HENLEY C. L., *Phys. Rev. Lett.*, **69** (1992) 3236.
- [14] WEIGERT S., *Europhys. Lett.*, **26** (1994) 561.
- [15] FRADKIN E., *Field Theories of Condensed Matter Systems* (Addison-Wesley, New York) 1991.
- [16] KOU S. P., LIANG J. Q., ZHANG Y. B. and PU F. C., *Phys. Rev. B*, **59** (1999) 11792.
- [17] MCLAUGHLIN D. W., *J. Math. Phys.*, **13** (1972) 1099.
- [18] PATRASCIOIU A., *Phys. Rev. D*, **24** (1981) 496.
- [19] WEISS U. and HAEFFNER W., *Phys. Rev. D*, **27** (1983) 2916.
- [20] DEL BARCO E., VERNIER N., HERNANDEZ J. M., TEJADA J., CHUDNOVSKY E. M., MOLINS E. and BELLESSA G., *Europhys. Lett.*, **47** (1999) 722.
- [21] GARANIN D. A., MARTÍNEZ-HIDALGO X. and CHUDNOVSKY E. M., *Phys. Rev. B*, **57** (1998) 13639.
- [22] CHUDNOVSKY E. M. and GUNTHER L., *Phys. Rev. Lett.*, **60** (1988) 661.
- [23] BOOTH I. S. and MANN R. B., *Phys. Rev. Lett.*, **81** (1998) 5052.